Solid-Propellant Burning-Rate Modification

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Low acceleration is one of the requirements for solid-propellant orbit insertion motors for future outer-planetary missions. This article describes the research accomplished in reducing the low-pressure burning rates of modified solid propellants. Techniques developed with the saturated hydroxy-terminated polybutadiene system were successfully applied to the polyether system (JPL 540) and an unsaturated hydroxy-terminated polybutadiene propellant system. Burning-rate reductions up to 50% were obtained by the synergistic effects of increased oxidizer size, reduction of iron, and inclusion of flame retardants and endothermic combustion modifiers.

Introduction

Spacecraft design studies at JPL, for future outer-planetary missions, have shown that low acceleration is one of the requirements for solid-propellant orbit insertion motors. A prerequisite for achieving these low-acceleration, high-performance solid-propellant spacecraft motors is the development of very low burning rate propellants with specific impulses equal to or better than the JPL 540 propellant. This work was conducted to investigate applicable methods of producing the necessary low-propellant burning rates without seriously degrading the efficiency of the combustion process. The study was concerned, primarily, with tailoring existing propellant formulations and, secondarily, with developing general techniques adaptable to alternate binder compositions.

Burning-rate tailoring began by studying the effects of modifications to the following propellant formulations: saturated hydroxy-terminated polybutadiene (SHTPB), polyether–polyurethane (JPL 540), and unsaturated hydroxy-terminated polybutadiene (UHTPB). These propellant systems were developed at JPL. The modifications investigated were oxidizer particle size, cure catalysts, binder ingredient alterations, and inclusion of combustion modifiers. The modified formulations of each

propellant system were mixed in 2-kg batch sizes in a 3785.4-cm^3 (1-gal)[1] Bramley mixer. The propellant batches were cast into Crawford bomb and soda straw burning-rate strands and physical property tensile bar molds. Based on the planetary mission low-acceleration requirements, an absolute combustion pressure of 68.9 N/cm^2 (100 psi) was chosen as the comparable parameter for the development.

Saturated Hydroxy-Terminated Polybutadiene System

An existing propellant system utilizing an SHTPB binder was the first system studied as a low burning rate propellant candidate. This propellant was selected since the standard formulation already had an inherently lower burning rate than JPL 540. This SHTPB binder, called Telagen S, was produced by the General Tire and Rubber Company. The propellant was modified by combinations of increased oxidizer particle size, an organo-phosphate flame retardant, and a low concentration of a gas producer. The results of these modifications indicated that the burning rate was lowered from a standard of 0.24 to 0.13 cm/s (0.094 to 0.052 in./s) at absolute pressure 68.9 N/cm^2 (100 psi). At the same time, changes in physical properties occurred, that is, the tensile strength decreased from a standard of 198.6 to 134.5 N/cm^2 (288 to 195 psi), and the elongation increased from a standard of 35 to 44%.

Since the SHTPB propellant system cures at 377.6 K (220°F) for five days, a study was performed to lower these cure conditions. Utilizing polymerization catalysts, a more rapid low-temperature cure of 300–305 K (80–90°F) for two days was obtained with small concentrations of ferric acetoacetonate (FeAA). However, it was found that the FeAA promoted increased burning rates. Examination of other organo-metal compounds, as potential cure accelerators, indicated that vanadium acetoacetonate (VaAA) would give the desired cure without alteration of the propellant burning rate or mechanical properties.

Soluble unreactive binder additives were also evaluated. The materials studied included: tri (bromo propyl) phosphate, tri cresyl phosphate (TCP), dihydro ethoxy trimethyl quinoline (ethoxyquin), octyl diphenyl phosphate (ODDP), and isodecyl diphenyl phosphate (IDDP). Only the IDDP was found to be effective in reducing the burning rate at a low concentration of 1%.

Polyether–Polyurethane System

Since JPL 540 propellant is well understood, it was also selected as a low-acceleration candidate propellant. The burning rate for the standard

[1]Where applicable, the International System of Units is stated first, followed by the customary units in parentheses. In each case, the value in parentheses represents the measured or calculated unit.

propellant formulation is 0.356 cm/s (0.140 in./s) at absolute pressure 68.9 N/cm^2 (100 psi). Modifications were made to this propellant system which resulted in a reduction of the maximum burning rate to 0.229 cm/s (0.090 in./s) at absolute pressure 68.9 N/cm^2 (100 psi). The modifications made were as follows:

(1) The average oxidizer particle size was increased from 185 to 340 μm.

(2) One percent of an organo-phosphate flame retardant was added.

(3) Regular aluminum powder (2000 ppm iron) was replaced with an essentially iron-free aluminum (20 ppm iron).

(4) Two percent oxamide was added.

Based on the data generated from the strand burning tests, a 2.95-kg (6½-lb) batch of the 0.229-cm/s (0.090 in./s) modified propellant system was loaded into a 12.7-cm (5-in.)-diameter motor. The motor was fired at an average absolute pressure of 62.7 N/cm^2 (91 psi), resulting in an average burning rate of 0.259 cm/s (0.102 in./s). The slightly higher rate was obtained by a reduction of the oxamide concentration to 1%.

Combustion rate studies performed by Rocketdyne, a Division of North American Rockwell Corporation, indicated the burning rate of JPL 540 at absolute pressure 68.9 N/cm^2 (100 psi) could be reduced from 0.356 to 0.196 cm/s (0.14 to 0.077 in./s) by replacing 10% of the oxidizer with nitroquanidine, in addition to the other modifications. No adverse effects in processing or mechanical properties were noted in the propellant; however, in firing the 5.08-cm (2-in.)-diameter motor configurations, a reduction in predicted specific impulse resulted.

Differential scanning calorimeter studies showed a dependence of burning rate on the iron concentration of uncured propellants. Based on this information and the effect of iron on SHTPB formulations, the effort was directed toward complete removal of iron from the propellant. If a minimum burning rate could be established in an iron-free environment, then iron could be quantitatively added to provide any desired rate. The cure catalyst used in 31 experimental batches of JPL 540 was FeAA. Other organo-metallic compounds were tested as replacements for this compound, but none would effect a complete propellant cure. Two metal chelates containing lead and titanium gave excellent cures in gum stock studies, but when combined into a propellant with oxidizer, they would not produce the same degree of cure. The synergistic effects of ammonium perchlorate oxidizer and cure catalyst, trace metals, or other components in the binder are little understood. Some ammonium perchlorate solubility in polypropylene glycol with dissociation is believed to take place as evidenced by the inactivation of metallic catalysts. Bonding

agents, such as the tertiary amines, MT-4, and dihydroxy propyl cyanoethyl amine (C-1), apparently reduced this effect. Oxamide, in low concentrations, was found to reduce the required concentration of the iron cure accelerator and may be functioning in the same manner.

To obtain information on the combined effects of ammonium perchlorate on the binder polymerization process and the burning rate alterations, propellant batches were made with more chemically basic binder insoluble additives, such as calcium oxide (CaO), magnesium oxide (MgO), and disodium phosphate ($NaHPO_4$). Calcium oxide, the more basic of the additives, prevented binder cure entirely, even in the presence of the FeAA cure catalyst. Magnesium oxide produced a soft cure with increased burning rates. Disodium phosphate allowed a cure but increased the burning rate and reduced the mechanical properties. Another binder insoluble material investigated, sodium fluoborate ($NaBF_4$), produced acceptable cures with decreased burning rates but also degraded the propellant strain capabilities. Of the insoluble materials examined, oxamide was the only one that did not alter the cure capability or degrade the mechanical properties while effectively contributing to reducing the burning rate. Of the soluble unreactive binder additives, only the IDDP material was evaluated, based on previous results in the polyether–polyurethane system. Due to the very low viscosity of IDDP, a thinner mix was produced which suggests the possibility of increasing the propellant total solids content.

Another method investigated to reduce the burning rate of the polyether binder system was to change the binder polymer structure. Major changes in the binder formulation were not attempted since little change from the low-modulus, high-elongation mechanical properties of JPL 540 could be tolerated. Since the molecular weight and functionality of the polyether monomer were fixed, the only available degree of freedom to investigate was the co-reacting low molecular weight polyols containing known flame suppressant functional atoms or groups.

It was also desired to raise the melting point, or thermoplastic point, of the polymer to increase the temperature required for combustion. Among the reactive materials investigated were brominated polyols, phosphated polyols, halogenated phosphated polyols, and hydroxy-terminated amines.

Burning rates were slightly reduced with the phosphated polyols; however, an unexpected rate increase was noted with a brominated polyol. The amines showed little or no influence in the low-pressure region (absolute) of 34.47 to 172.35 N/cm^2 (50 to 250 psi). A linear aliphatic diisocyanate (DDI) was compared with the aromatic toluene diisocyanate (TDI) as a chain extender, but no improvements were detected in either the strain capability or burn-rate reduction.

Unsaturated Hydroxy-Terminated Polybutadiene System

The third propellant system investigated was an experimental propellant containing a UHTPB binder. This system is an attractive low-acceleration propellant candidate due to its inherent low burning rate characteristics. Also, it has a high solids loading capability and potentially can be cured at or near room temperatures.

An exploratory series of fifteen 3785.4-cm^3 (1-gal) batches of propellant were made with UHTPB. Although the results of the first series did not produce a high strain capability, low burning rates at absolute pressure 68.9 N/cm^2 (100 psi) were achieved. Initially, a tin cure accelerator was used but reaction rates were so rapid that polymerization occurred during the mix cycle. Complete elimination of the cure accelerator did not sufficiently reduce the reaction rate to allow casting. Inclusion of the antioxidant phenyl beta naphthyl amine (PBNA) at 1% by weight of UHTPB helped reduce the reaction rate. The addition of 2% by weight of diethanol amine stearate further reduced the reaction rate and also helped to internally plasticize the mix. However, larger quantities of the stearate tended to cause gellation, probably due to the amine reaction. A very good polymerization was obtained when DDI was substituted for TDI as the chain extender. Batches made using a plasticizer, dioctyl adipate (DOA) at 20 to 25% by weight of the binder, produced very fluid mixes which were easily processed at 86% solids loading. Burning rates for UHTPB formulations containing 82% solids were found to be 0.18 to 0.213 cm/s (0.071 to 0.084 in./s) at absolute pressure 68.9 N/cm^2 (100 psi). These rates were accomplished by using 340-μm ammonium perchlorate, a phosphated polyol, iron-free aluminum, and IDDP. One formulation containing a low molecular weight polyol, bis-hydroxy propyl aniline (Isonol C-100), gave a burning rate of 0.165 cm/s (0.065 in./s) at absolute pressure 68.9 N/cm^2 (100 psi) and a maximum stress of 186.2 N/cm^2 (270 psi) with a strain of 27% as determined from tensile specimens. Use of the ammonium perchlorate bonding agent MT-4 did not improve the strain capability of this propellant. Several hydroxy-terminated materials were co-reacted with the UHTPB in an effort to improve the strain capability but with little success. Straight UHTPB without reactive modifiers produced propellants with 5–7% strain capabilities and burning rates of 0.198 to 0.218 cm/s (0.078 to 0.086 in./s) at absolute pressure 68.9 N/cm^2 (100 psi). Use of stearates in the formulations increased the strain level to 17% without affecting the burning rate.

Conclusions

The most significant reduction in propellant burning rates was obtained by increasing the average particle size of the oxidizer. This was generally true for each binder system studied. Additional reductions in burning rates were obtained by incorporating binder soluble organo-phosphates and the binder insoluble oxamide. These modifications were made more

effective by the reduction in overall iron content of the propellant systems. Preliminary studies with the unsaturated hydroxy-terminated polybutadiene system showed promise as a low burning rate, advanced urethane-type binder.

It was demonstrated that low burning rate propellant systems could be developed without seriously degrading the standard physical property characteristics.